Short Communication

ESR spectroscopic study on the incorporation of Fe(III) into Li_2O–Al_2O_3–B_2O_3 glasses

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The X band ESR spectra at 77 and 300 K of $Li_2O-Al_2O_3-B_2O_3$ glasses investigated comprize four resonances, which can be assigned to Fe^{3+} ions brought into the samples by the raw materials, mainly by alumina. Signals at $g' = 3$, 2.3, 2.07 are due to Fe^{3+} ions incorporated into an autonomous Fe_xO_y phase or respective cluster-like precursors.

The amplitude of the $g' \approx 4.3$ signal typical for the Fe^{3+} ion in oxidic glasses corresponds with the Li_2O content of the glasses. This indicates that the Fe(III)/Σ Fe ratio is mainly influenced by the ability of the Li^+ ion to stabilize $[FeO_{4/2}]^-$, i.e., four-fold coordinated Fe(III) can only be stabilized if the Li^+ content of the glasses is sufficiently large.

ESR-spektroskopische Untersuchung des Fe(III)-Einbaus in Li_2O–Al_2O_3–B_2O_3-Gläser

Die bei 77 und 300 K aufgenommenen X-Band-ESR-Spektren von $Li_2O-Al_2O_3-B_2O_3$-Gläsern weisen vier verschiedene Signale auf. Diese sind Fe^{3+}-Ionen zuzuordnen, die über die Rohstoffe, insbesondere über Aluminiumoxid, in die Gläser gelangen. Die beobachteten Signale bei $g' = 3$; 2,3 and 2,07 sind auf Fe^{3+}-Ionen in einer autonomen Fe_xO_y-Phase oder entsprechenden clusterartigen Vorstufen zurückzuführen.

Die Amplitude des für das Fe^{3+}-Ion in oxidischen Gläsern typischen Signals bei $g' \approx 4,3$ korrespondiert mit dem Li_2O-Gehalt der Gläser. Das Fe(III)/Σ Fe-Verhältnis wird wesentlich durch die Fähigkeit des Li^+-Ions, $[FeO_{4/2}]^-$ zu stabilisieren, beeinflußt, d. h., vierfach koordiniertes Fe(III) tritt nur in Gläsern mit einem hinreichend großen Lithiumgehalt auf.

1. Introduction

Though, as a result of numerous studies, it is generally accepted that the Fe(II)/Fe(III) ratio and the symmetry and coordination numbers of these ions in glasses are determined by the chemical composition and the preparation techniques used as well, many questions remained unanswered up to now. This is due to a lack of knowledge about the interdependence between glass structure and iron incorporation. This situation may become further complicated by the tendency of iron to form clusters or precursors of autonomous Fe_xO_y phases.

Aluminoborate glasses are interesting objects to study the incorporation of Fe(III) into glassy networks since ferric ions can occupy $[AlO_4]$ and $[AlO_6]$ sites identified ^{27}Al-NMR-spectroscopically without any doubt [1].

2. Experimental

The glasses were prepared by melting Li_2O, Al_2O_3 and H_3BO_3 in platinum crucibles using an electrically heated furnace. Depending on composition temperatures between 1050 and 1300 °C were applied and the samples were carefully cooled down from transformation region. The glass-forming region of this system is limited by phase separation as indicated in figure 1.

Among the starting materials used for the synthesis of the glasses Al_2O_3 acts as the main Fe(III) source due to the comparable ionic radii of Fe^{3+} and Al^{3+} ions. This was checked by chemical analysis and ESR spectroscopic study of the raw materials. During the melting process the coordination number of a part

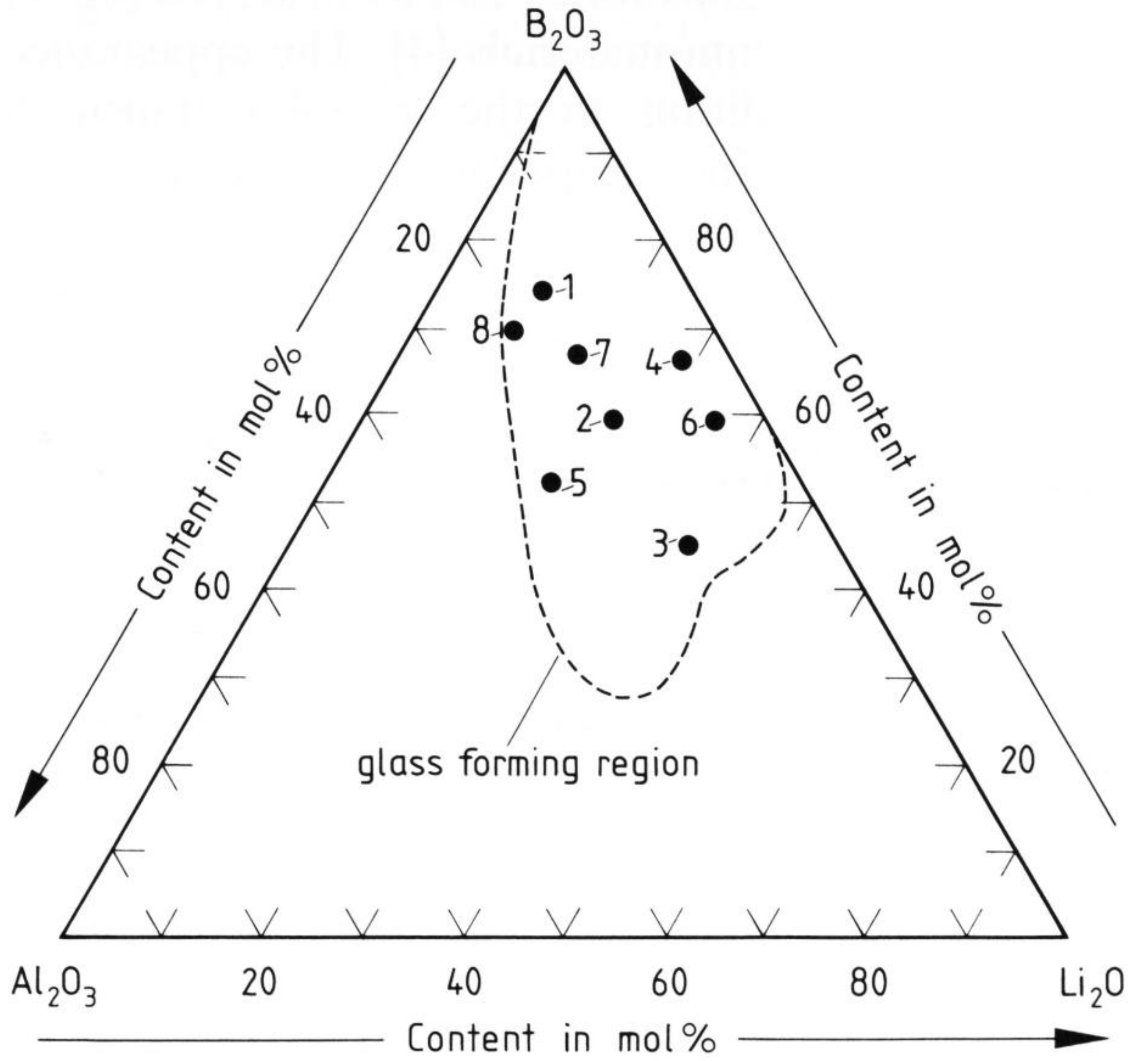

Figure 1. Compositions of investigated samples (according to [2]).

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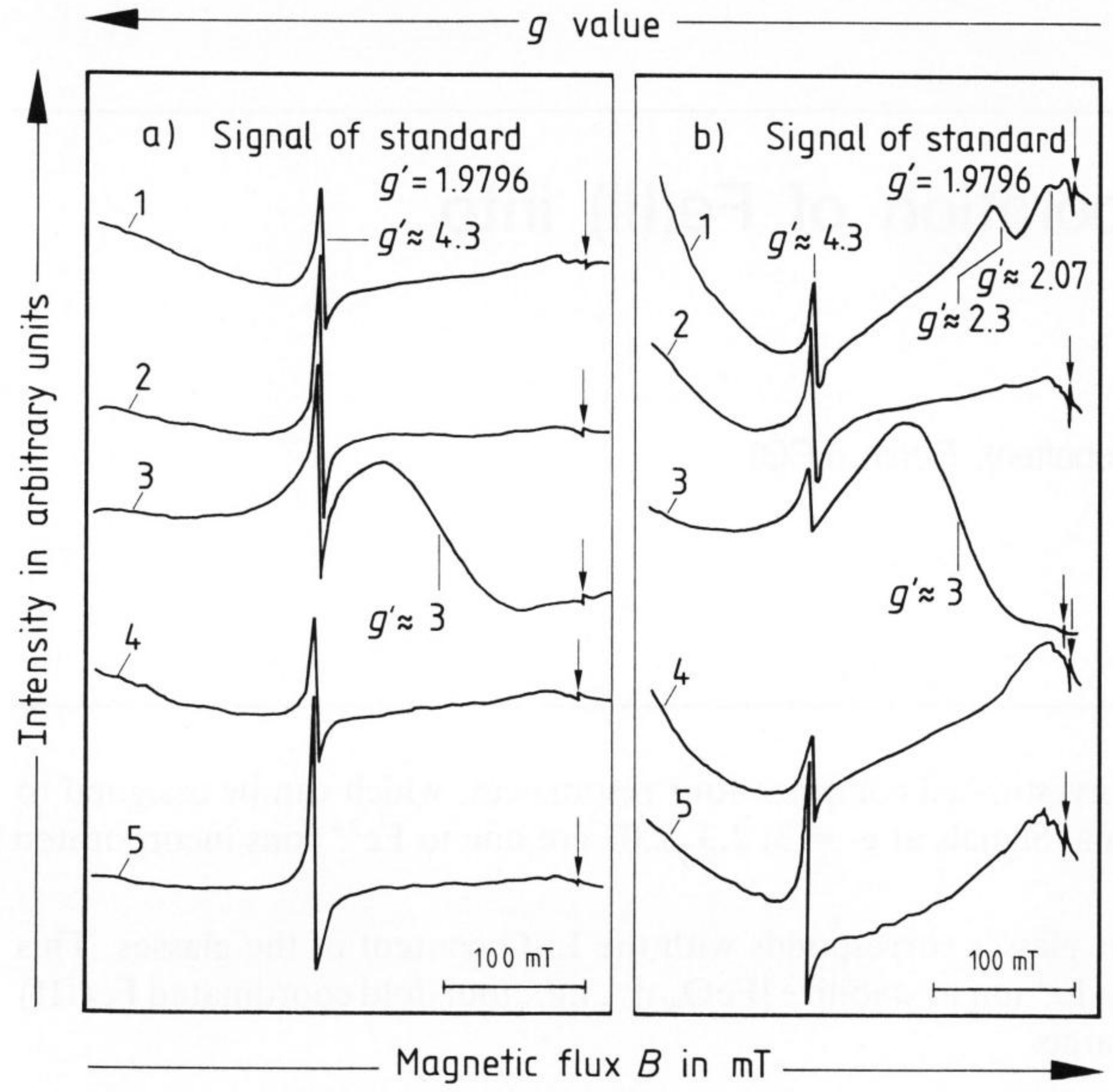

Figures 2a and b. ESR spectra of glass samples no. 1 to 5 recorded at 77 K (figure a) and at 300 K (figure b), respectively. ↓ indicates the signal of the standard, $g' = 1.9796$.

of the Al^{3+} ions decreases from 6 (in corundum) to 4 (as found in the glassy samples); boron appears to be 3- and 4-coordinated also in these glasses.

3. Results and discussion

Figure 1 shows the compositions of samples no. 1 to 8 (in mol%) and figures 2a and b show selected ESR spectra (X band) recorded at 77 K (figure 2a) and 300 K (figure 2b) observed in the B_0 range $0 \leq B_0 \leq 0.4$ T. Besides the $g' \approx 4.3$ resonance typical for Fe^{3+} ions in glasses [3] further signals appear at $g' = 3$, 2.3, and 2.07. The broad resonance at $g' \approx 3$ (sample no. 3) is due to Fe^{3+} ions incorporated into an autonomous Fe_xO_y phase or respective cluster-like precursors. Similar Fe^{3+} species are also responsible for the $g' \approx 2.3$ signals which can be observed e.g. in fusion-cast corundum materials [4]. The appearance of signals in addition to the $g' \approx 4.3$ transition indicates that the respective (especially the B_2O_3-rich) samples could not be obtained completely homogenously. Otherwise the following discussion of the $g' \approx 4.3$ signals will show that the percentage of additional phases in the samples under investigation is very small.

The $g' \approx 4.3$ resonance is often, on the basis of empirical arguments, assigned to $[FeO_{4/2}]^-$ [5] but can, taking into account the symmetry of the respective sites, also be due to the six-fold coordinated Fe^{3+} ion [6].

In table 1 the following data are collected for samples no. 1 to 8 (see figure 1): the chemical composition, the $g' \approx 4.3$, A, amplitudes (at 77 and 300 K) per mole of glass and per mole of Al_2O_3, respectively, the ratio of the amplitudes at 77 and 300 K.

If the Al_2O_3 content (and thus the iron source) is kept constant (series 1, 2, 3), then the $g' \approx 4.3$ signal amplitude increases with increasing percentage of Li_2O. The $[AlO_6]:[AlO_4]$ and $[BO_3]:[BO_4]$ ratios increase in the same order [1]. This allows to draw the conclusion that Li_2O allows larger Fe(III)/Σ Fe ratios and supports the formation of $Li[FeO_{4/2}]$ complexes, i.e. 4-fold coordinated Fe(III).

For the samples no. 2, 4, and 5 the Li_2O/B_2O_3 ratio is kept constant and the alumina content increases in the given sequence. Hence, the iron content of the glasses increases and the amplitude of the $g' \approx 4.3$ signal per mole glass increases (there is only a small change in the line width and form). If this amplitude is referred to the Al_2O_3 content of the glasses, i.e. to the iron content brought into the glasses via that raw material, then it decreases in the sequence given. Collecting these findings and arguments the following conclusion appears to be justified: Though in the series 2, 4, 5 the total amount of iron in the glasses increases (with increasing Al_2O_3 content) a decreasing part of this contributes to the $g' \approx 4.3$ signal. Thus, it was found for both series (1, 2, 3 and 2, 4, 5) that four-fold coordinated Fe(III) can only be stabilized if the Li^+ content of the glasses is sufficiently large. This conclusion also corresponds

Table 1. Compositions, $g' \approx 4.3$ amplitudes (in arbitrary units), amplitude ratios and additional resonances for glass samples no. 1 to 8

sample no.	compositions in mol%			amplitude per mole glass at		amplitude per mole Al_2O_3 at		ratio $A^{77\,K}/A^{300\,K}$	additional resonances
	Li_2O	Al_2O_3	B_2O_3	77 K	300 K	77 K	300 K		
1	10.0	15.0	75.0	5.76	1.55	0.38	0.10	3.7	2.075 2.338
2	25.0	15.0	60.0	10.35	2.11	0.69	0.14	4.9	–
3	40.0	15.0	45.0	13.59	2.34	0.91	0.16	5.8	3
4	28.5	5.0	66.5	6.60	1.15	1.32	0.23	5.7	–
5	22.5	25.0	52.5	13.28	2.71	0.53	0.11	4.9	–
6	35.0	5.0	60.0	6.40	1.16	1.28	0.23	5.5	–
7	17.5	15.0	67.5	11.50	2.69	0.77	0.18	4.3	2.075
8	10.0	20.0	70.0	7.38	1.94	0.37	0.10	3.8	2.075

with the ^{27}Al-NMR spectroscopic result that for series 2, 4, 5 the percentage of the six-fold coordinated Al^{3+} ion increases with increasing alumina content.

A final comment concerns the ratios of the $g' \approx 4.3$ amplitudes for the signals obtained at 77 and 300 K (A^{77}/A^{300}). This ratio should be equal to 3.8 if the Curie law would hold and no temperature-induced structural changes appear. For the $Li_2O-Al_2O_3-B_2O_3$ glasses under investigation these ratios are equal or greater than 3.8 and increase with increasing Li_2O content. This corresponds with the already mentioned influence of the Li^+ ion and supports the hypothesis that structural changes play a decisive role.

4. References

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